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14. ABSTRACT

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INITIATION AND DECOMPOSITION OF GREEN ENERGETIC MATERIALS

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Abstract

Recently there has been increased interest in high nitrogen content "green" energetic materials which are designed to produce relatively non-toxic decomposition products as part of a push to decrease the environmental impact of energetic materials through all phases of their existence. With the use of a T-Jump/Time-of-Flight Mass Spectrometer (T-Jump/TOFMS) capable of high heating rates (up to 10^6 K/s), and rapid sampling (resolution = 100 µs), we were able to probe the initiation and decomposition of these green energetics. The samples include 5-amino-1-methyl-1H-tetrazolium dinitramide (MeHAT_DN), 1,5-diamino-4-methyl-1H-tetrazolium dinitramide (MeDAT_DN), 1,5-diamino-1H-tetrazolium nitrate (DAT_N), 1,5-diamino-4-methyl-1H-tetrazolium azide (MeDAT_N3), and 5-aminotetrazolium dinitramide (HAT_DN), and were produced by the Kalpötke group of the Ludwig-Maximilian University of Munich. These materials have the commonality of a tetrazole containing cation species that is paired with a variety of anion structures. During rapid heating there are observed two competing breakdown mechanisms for the cation's tetrazole ring. There does not appear to be a correlation between the ring breakdown mechanisms and decomposition temperature, but rather with the placement of functional groups along the tetrazole ring. Since the tetrazole structure is a large part of each of these materials, the neutral 5-amino-1H-tetrazole (5-AT) was also tested to compare the decomposition between neutral and ionic species. Decomposition temperature and reaction time within the mass spectrometer are also determined, and for a few materials with slower reaction rates, multiple mechanistic steps can be observed. In a complimentary study several of these materials were tested on a micro-DSC device developed at the National Institute of Standards and Technology (NIST). Due to its small size, this system allows for rapid heating of samples and further investigation of the decomposition temperature and calculation of kinetic parameters under high-heating conditions.

Introduction

Recently, a shift has been made to create energetic materials (EMs) which are not only efficient performers, but also meet new safety and environmental standards. Current EMs such as RDX meet performance needs, but are sensitive to impact and friction, and produce environmentally harmful product species during the production and combustion processes. So called "green energetic materials" (GEMs) are produced with concern towards environmental impact throughout the lifetime of a material. Many of these compounds contain a tetrazole sub-structure, which is considered a high-nitrogen content material. The tetrazole structure can be given a positive charge and paired with a functional anionic molecule to form stable energetic salts. These materials are unique in that their energy release comes primarily from the high heats of formation from their many nitrogen containing bonds.[1] The high nitrogen content generally produces more environmentally friendly combustion products due to the diminished carbon containing product species. However, these materials are relatively new and have not been as extensively studied as more traditional EM's. Therefore, the decomposition products and reaction pathways are for the most part, still unknown. Several groups have performed experimental and theoretical work to help understand the thermal decomposition of aminotetrazole containing materials.[1-9] Tools ranging from thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and FTIR/TOF mass spectrometry have been used, but traditionally these experiments are performed under low heating rates (10-100 K/min). Under rapid-heating conditions closer to that of a real-time combustion event, there will typically be a different set of dominant chemical processes than at slow heating rates. Chowdhury *et al* used a confined rapid thermolysis technique to investigate the reactions of tetrazole based ionic liquids at heating rates of up to 2000 K/s. The main diagnostic tools for this study were FTIR spectroscopy and TOF spectrometry which obtained temporal resolutions of 50ms and 1ms, respectively.[5] They showed that positions of functional groups on the tetrazole ring play a significant role on the thermal stability and decomposition pathway of the tetrazole structure. Temperature-Jump FTIR/Spectroscopy with a heating rate of 2000 K/s was used by Brill *et al* to investigate the reaction pathways of aminotetrazole and a few of its related salts.[7] They identify two possible reaction pathways that vary with temperature; one which is dominant at low temperatures and consists of the breakdown of the ionic tetrazole structure, and one which is dominant at high temperatures and treats the aminotetrazole as a neutral. The main identifying products of these two pathways are HN_3 for the high temperature pathway and N_2 for the low temperature pathway. Theoretical work has been performed by Paul *et al* on unimolecular 5-aminotetrazole decomposition.[4] Their studies also reveal two

possible decomposition pathways for the tetrazole structure, which differs for the amino and imino tetrazole forms. They predict that the main aminotetrazole reaction pathway will be that of N_2 extraction, while the main iminotetrazole pathway will be that of HN_3 removal.

In general, it has been shown that the decomposition of the tetrazole molecule can differ due to the placement and nature of its attached functional groups. It is also predicted that heating rate will have an effect on the decomposition. The majority of the previous work has been performed at low heating rates or at high heating rates with slow sampling times when compared to characteristic reaction timescales.. In order to investigate the intermediate processes of a reaction, an experiment with very high heating and sampling rates is required. In this paper we employ a Temperature-Jump/Time-Of-Flight Mass Spectrometer to characterize the decomposition pathways of several aminotetrazole containing energetic salts. The uniqueness of this instrument is its ability to heat samples at very high heating rates of $\sim 10^6$ K/s while simultaneously sampling the reaction products at a temporal resolution of 100 µs, which can allow for probing of the early stages of reaction.

Several groups have characterized high-nitrogen energetics via DSC and related experiments. 5-aminotetrazolium nitrate[2], 1,5-diamino-4-methyl-1*H*-tetrazolium nitrate[9], 1,5-diamino-4-methyl-1*H*tetrazolium dinitramide[9], 1,5-diamino-4-methyl-1*H*-tetrazolium azide[9], and 5-aminotetrazolium dinitramide[10], are just a few examples of ionic salts that have been characterized by standard DSC methods. In addition to decomposition temperature, activation energy can also be determined by varying the heating rate and using iso-conversion techniques like those by Ozawa[11] or Kissinger[12]. Ma *et al* performed this experiment for 5-aminotetrazolium nitrate from (2 to 25) K/min and obtained an activation energy of 303.2 kJ/mol using the Ozawa method and 311.0 kJ/mol using the Kissinger method. In a similar DSC experiment at heating rates of (2 to 40) K/min Fischer *et al* determined the activation energy of several ionic salts and found them to be in the range of $\sim$(101 to 138) kJ/mol using both the Ozawa and Kissinger methods.[9] Relative to heating rates commonly experienced during combustion of energetic materials, traditional DSC heating rates are many orders of magnitude lower. To achieve very high heating rates that approach those that are relevant to energetic materials, new classes of DSC devices are necessary. These new devices based on MEMS fabrication methods offer very fast response due to the small thermal mass of the heaters and sample size.[13-16] A micro-DSC device previously developed at the National Institute of Standards and Technology (NIST) is capable of heating rates up to 1×10^7 K/s,[16] and was previously used to explore phase changes in Ni/Si thin films.[17] In this study this device is used to investigate the decomposition temperature and activation energy of several high-nitrogen energetic salts and results are compared with that of traditional DSC.

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Experimental

The primary experimental device is a Temperature-Jump/Time-Of-Flight Mass Spectrometer (T-Jump/TOFMS), which has been described in detail elsewhere.[18] The core of this instrument is a fine platinum filament of ~76 µm in diameter and 1-2 cm in length. This filament can be heated at very high rates of up to 10^6 K/s using a tunable current pulse. Samples are received in a solution of ethanol or methanol, and are placed onto the sampling probe by manually applying a drop of the solution to the platinum wire. All samples used in this experiment are provided by T.M. Klapötke of Ludwig-Maximilians University in Munich, Germany, and consist of 5-amino-1H-tetrazole (5-AT), 5-amino-1-methyl-1*H*-tetrazolium dinitramide (MeHAT_DN), 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide (MeDAT_DN), 1,5-diamino-1*H*-tetrazolium nitrate (DAT_N), 1,5-diamino-4-methyl-1*H*-tetrazolium azide (MeDAT_N3), and 5-aminotetrazolium dinitramide (HAT_DN).   The synthesis of each material is documented elsewhere with the exception of 5-aminotetrazole which was acquired from Sigma-Aldrich.[1, 6, 10, 19] For sampling purposes, the filament is placed in close proximity (~1 cm) to the ionization source, a 70 eV electron impact beam. This allows for reaction products to reach the MCP detector of the mass spectrometer at a fast time scale below that of the characteristic reaction time. A typical heating run consists of a ~3 ms heating pulse which heats the filament up to ~1970 K or a rate of ~560,000 K/s. Throughout the heating of the sample, a mass spectrum is taken every 100 µs, and the current and voltage are simultaneous recorded to calculate the temperature of the filament.

In a complimentary experiment, 5-AT, MeHAT_DN, MeDAT_DN, and MeDAT_N3 were tested with a high heating rate micro-differential scanning calorimeter (µ-DSC) shown in Figure 1.[16] Small quantities of the samples are placed on to the device using a PV820 Pneumatic Pico-pump system (World Precision Instruments)[20] capable of producing pico-liter sized drops. Due to the small size of the µ-DSC, rapid heating rates ranging from ~4000 to ~115,000 K/s are possible. Calibration was performed to confirm the temperature of the heating surface using three samples with well documented phase change points, tin, potassium perchlorate ($KClO_4$), and potassium nitrate (KNO_3), which has two calibration points. The known calibration points were the melting point of tin at 505 K [21], a crystalline phase shift of $KClO_4$ at 572 K [22], a KNO_3 crystalline phase shift at 401 K [22, 23], and melting at 607 K [24]. For each material the activation energy under high heating rates was determined using the Kissinger Method,[12]

$$\ln\left(\frac{\beta_i}{T_{p,i}^2}\right) = Constant - \frac{E_a}{RT_{p,i}} \qquad (1)$$

4

where β is the heating rate, T_p is the peak temperature of the calorimetric trace, and E_a is the activation energy.
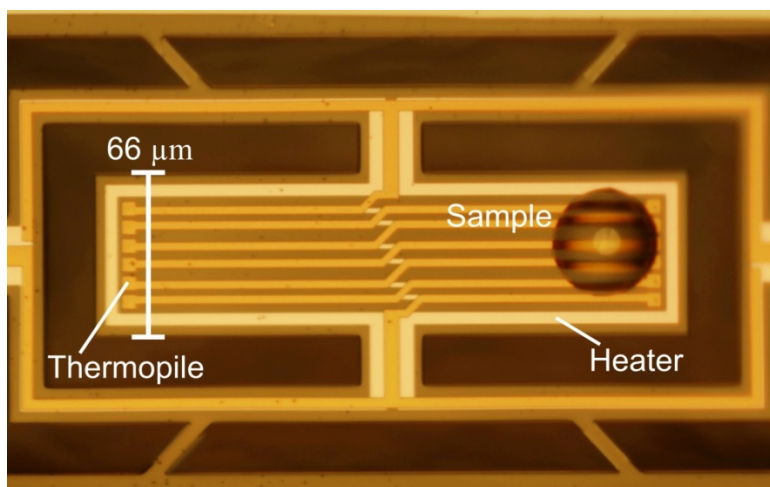

Figure 1: Image of microcalorimeter with a droplet of an organic energetic sample.

Results and Discussion

Decomposition temperatures and reaction times for the six compounds were determined from mass spectrometer results at a heating rate of ~560,000 K/s and are tabulated in Table 1. The decomposition temperatures were taken from the onset of product species, and the reaction times were determined from the full-width half-max of the product species concentration. In the following we explore the individual decomposition behavior of each compound.

Compound	Decomposition Temperature (K)	Reaction Time (ms)
5-AT	573	0.3
MeHAT_DN	633	0.3
MeDAT_DN	833	0.2
DAT_N	583	0.5
MeDAT_N3	583	0.4
HAT_DN	693	0.7

Table 1: Measured decomposition temperature and reaction time.

<u>5-amino-1H-tetrazole</u>

The thermal decomposition of tetrazole containing energetic salts can be a complex process.. Therefore, to gain knowledge on the breakdown of the tetrazole structure under high heating rates in vacuum, we first examine the fairly simple molecule of 5-AT, **1**. The major product species detected by the T-Jump/TOFMS during

decomposition can be seen in Figure 2. The major product species are at a mass to charge ratio (m/z) of 28, 29, and 57, while peaks at 17 and 18 represent background species.
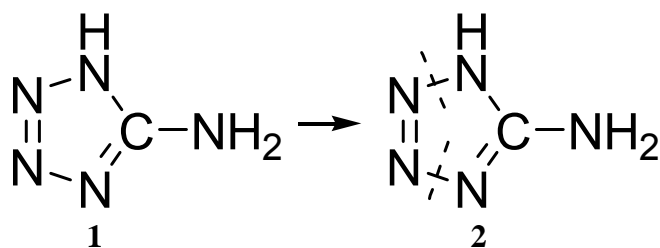
There is also a small background peak at m/z 28, but considering the intensity of the peak at m/z 28 due to the product species, we consider the background at this m/z negligible. If we examine the 5-AT molecule and assume that the initial breaking of the molecule will occur at the N-N or C-N single bonds rather than at any double bonds, we can predict the molecule to break at the N-N single bonds as shown in **2** to form the product species at m/z 28 (N_2) and 57 (CH_3N_3). To form m/z 29 we expect that the CH_3N_3 fragments during ionization to form m/z 28 and 29 along with m/z 57.   In their unimolecular decomposition work, Paul *et al* observed several possible decomposition pathways for 5-aminotetrazole.   One proposed pathway leads to mass 28 and 57 that is consistent with our experiment and shows isomerization of the CH_3N_3 fragment leading to the reaction products shown in **3**. However, experiments have often shown 5-AT decomposing in a different manner with HN_3 as a primary reaction product.[3, 7, 25]
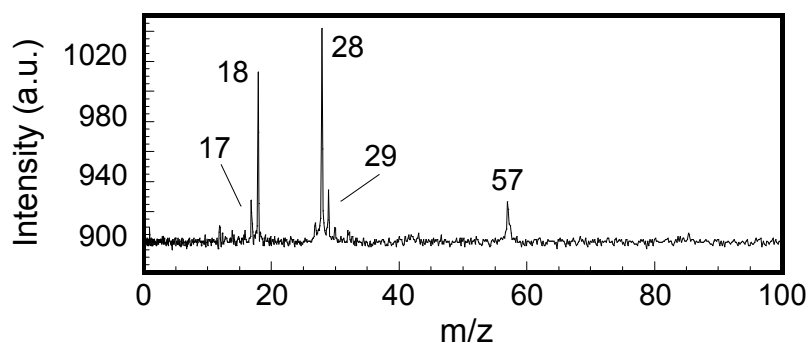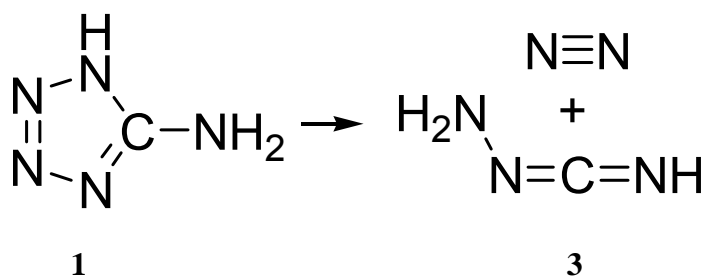

Figure 2: Detailed mass spectrum for 5-AT, **1**.

The presence of HN_3 could be due to several experimental differences from the current study, mainly in that sampling was performed at higher pressures and longer time scales so that secondary gas phase reactions are possible. HN_3 could also be due to the presence of the tautomer of 5-AT, 5-iminotetrazole, **4**. Work by Levchik and Lesnikovich has shown that despite being named 5-aminotetrazole, the material is often composed of both 5-aminotetrazole and 5-iminotetrazole in the solid state.[3, 25] They conclude that HN_3 is due to the breakdown of the imino form, and breakdown of the amino form results in N_2 and CH_3N_3 as detected in our study. Lesnikovich and Levchik also note that the imino form will tautomerize to the amino form during heating. Absence of HN_3 in our study could be a result of the rapid heating conditions that are used in our experiment. If the tautomerization of the imino form to the amino form occurs faster than the kinetics of decomposition of the iminotetrazole, then our study would probe the reaction of the amino form.
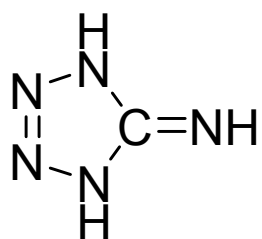
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5-aminotetrazolium dinitramide

The cation of 5-aminotetrazolium dinitramide (HAT_DN), **5**, contains the same basic tetrazole structure as 5-AT with an added proton to the tetrazole ring and is paired with the dinitramide ($N_3O_4^-$) anion. The addition of the dinitramide anion significantly increases the complexity of the molecule and the decomposition pathway. Of the molecules studied, this has the slowest reaction time (see Table 1), which allows for the capture of multiple steps within the reaction that may not be detectable for other materials. Figure 3 shows a single detailed spectrum for **5**, which shows the increased number of product species when compared to **1**. If we apply the same N_2 expulsion mechanism as in **1→3**, we would expect m/z 57 and 28 as in the neutral 5-aminotetrazole case, which are observed. However, it appears that this mechanism is not sufficient to describe the decomposition of **5**.
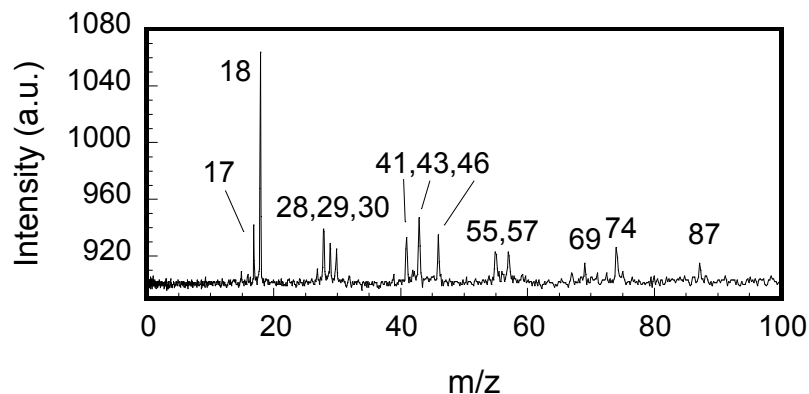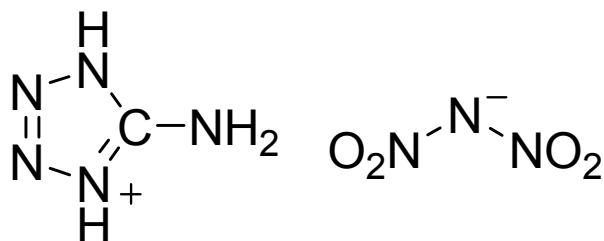
Figure 3: Detailed mass spectrum for HAT_DN, 5.

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For diagnostic purposes, we consider that the cation and anion decompose independently. For the largest mass observed, m/z 87, we note that the cation of 5 has a molecular mass of 86. Paul *et al* suggests that there is an intermediate step in the reaction of the tetrazole structure where the ring first splits before N_2 is released as shown by 6.[4] The work by Paul is a theoretical unimolecular decomposition study, so it is unable to predict intermolecular hydrogen exchange. We assume that with the ionic nature of this material there is some exchange of hydrogen atoms between molecules. As the tetrazole ring splits apart by breaking an N-N bond, it is reasonable to assume that protonation of the open ring could occur to form a structure similar to 7 with m/z 87, which is consistent with our observation.
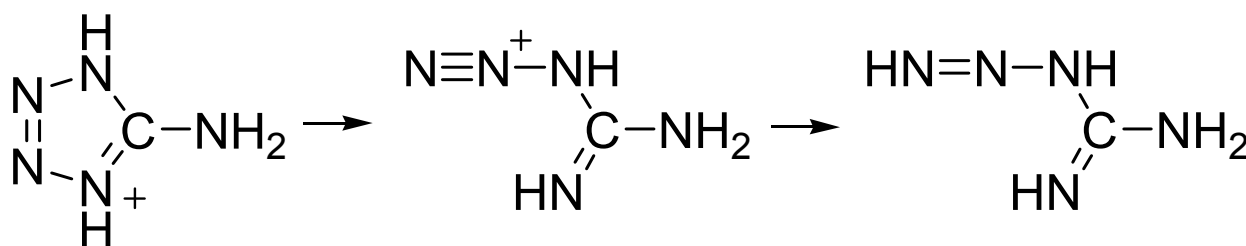
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The other large molecule detected by our system, m/z 74, has not been previously reported in the literature as a decomposition product of tetrazole or dinitramide reactions, and may represent an intermediate step in the initial

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reaction process. It is difficult to create m/z 74 from the tetrazole containing cation without significant recombination and intermixing with the anion or without the addition of several hydrogen atoms. Since this experiment is performed at a fast time scale under vacuum, we assume this is not occurring and that mass 74 is being produced from the dinitramide anion. With a molecular mass of 106 the dinitramide molecule can form m/z 74 through the loss of 2 oxygen atoms. Examining the dinitramide structure **8** proposed by Bottaro *et al*, [26] we predict a loss of $2O^-$ to form N_3O_2. N_3O_2 has been experimentally observed in positive[27, 28] and negative[29] ionic forms, but to our knowledge, not as a neutral molecule., Although the neutral molecule has not been experimentally observed, theoretical work has shown that this formation is possible, but thermodynamically unstable.[30] Regardless of overall charge, there is evidence that N_3O_2 will decompose to NO and N_2O.[31-33]
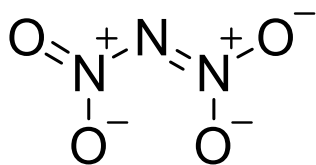
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Figure 4 shows the temporal evolution of select product species pertaining to the decomposition of the dinitramide structure. The earliest species observed are m/z 74 and m/z 46, where m/z 46 represents NO_2, a common decomposition product of N_3O_4 containing compounds.[26, 34] The presence of these two reaction products suggests that there may be competing mechanisms for decomposition. There has been previous reports of two different mechanistic pathways for dinitramide breakdown in an Ammonium Dinitramide compound.[34-36] The two pathways consist of a low temperature NO_2 forming pathway, and a high temperature N_2O forming pathway. These two mechanisms are consistent with what we observe, as NO_2 is present at a lower temperature, followed by the appearance of N_2O (m/z = 44) at a higher temperature. These two mechanisms are both at play within this system, and m/z 74 may be a part of an intermediate step in the high temperature reaction. While peaks 46, 44, 30, can all be attributed to the dinitramide breakdown, peak 30 is due to several species.   There are three contributions to the detected NO concentration in HAT_DN decomposition, production of NO from the reaction itself as well as from fragmentation of N_2O and NO_2. Based on fragmentation patterns obtained using neat NO_2 and N_2O gas, we conclude that at low temperatures the majority of the NO is produced from NO_2 fragmentation, while at higher temperatures NO is directly formed from the decomposition process, possibly from N_3O_2 decomposition.
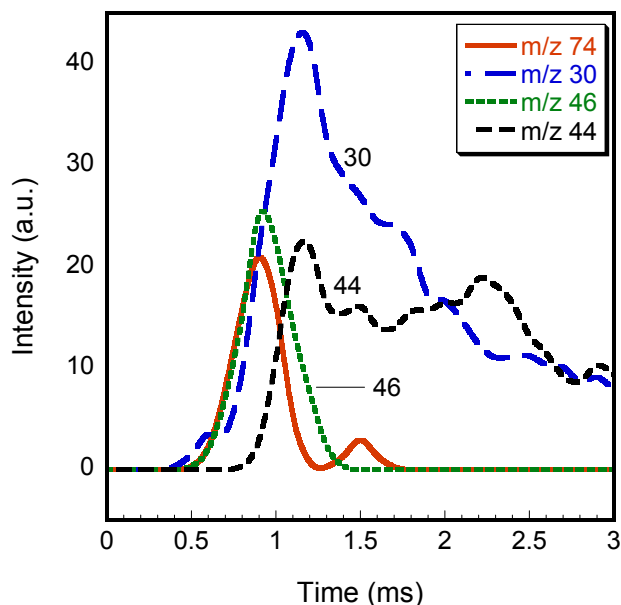
Figure 4: Detected product species during heating of **5**.

As with the dinitramide structure, it can be assumed that there are multiple pathways at play for the tetrazole molecule. If the tetrazole ring broke as shown in **9**, the products would likely be HN_3 and CH_3N_2, both m/z 43 and present in Figure 3. . Other species can be attributed to electron impact fragmentation or hydrogen mobility between molecules. CHN_3 is a likely candidate for m/z 55, which could be formed from hydrogen loss from m/z 57, or from fragmentation during ionization of m/z 87. The same situation holds for mass 41, which is likely to be CHN_2 from fragmentation of CHN_3 or m/z 87. We attribute mass 29 to HN_2, but its appearance in the spectrum for aminotetrazole suggests it could be a result of fragmenting during ionization of m/z 57.

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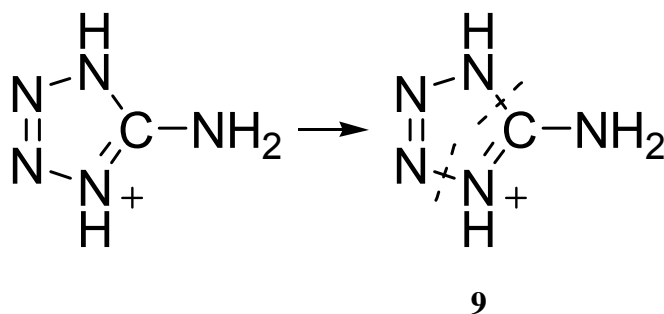
5 -amino-1-methyl-1H-tetrazolium dinitramide

The structure for MeHAT_DN is shown in **10** and a sample spectrum is shown in Figure 5. This structure is very similar to **5** except one hydrogen atom on the tetrazole ring is replaced with a methyl group. If we first compare this decomposition with that of 5-aminotetrazole, we notice that there is no peak at m/z 57.
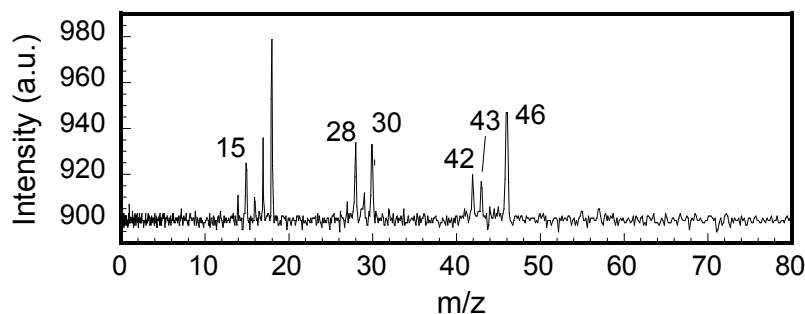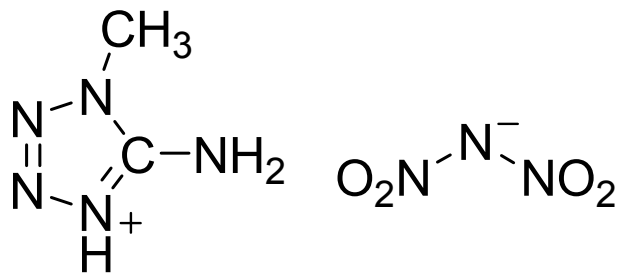
10

**Figure 5:** Detailed mass spectrum of MeHAT_DN, **10**.

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This suggests that the addition of the methyl group has a significant impact on the decomposition of the tetrazole ring. We observe m/z 15, corresponding to the methyl group, which suggests that this structure easily breaks off of the tetrazole ring. If the decomposition of the tetrazole ring follows that of **2**, the remaining fragment should have a mass of 57. However, the lack of m/z 57 implies some other pathway, likely that of **9**. Pathway **9** should lead to CH_3N_2 and CH_3N_3 which can further decompose to form the products in **11**, that are observed through m/z 15 (CH_3), andm/z 42 (N_3). The tetrazole ring breaking in **9** is similar to part of the decomposition for HAT_DN as this material also formed CH_3N_2 (m/z 43), but there are many differences in the decomposition of these two materials. Peaks 87, 74, 57, 55, 44, and 41 were present in the HAT_DN decomposition, but are not present in the decomposition of **10**. As mentioned previously, for both the dinitramide and tetrazole structures there are at least two possible breakdown mechanisms. The addition of the methyl group to the tetrazole ring appears to change the breakdown mechanism to form HN_3 rather than the N_2 and CH_3N_3 as was seen for 5-AT . The absence of other product species can also be attributed to this differing mechanism in the tetrazole ring breakdown. For the dinitramide decomposition in HAT_DN we assumed a high temperature N_2O forming route, and a low temperature NO_2 forming route. Since N_2O is absent in this system we can conclude that we are observing the low temperature dinitramide decomposition. We predict that mass 74 is a precursor to the production of N_2O in the high temperature mechanism, and this species is also missing.
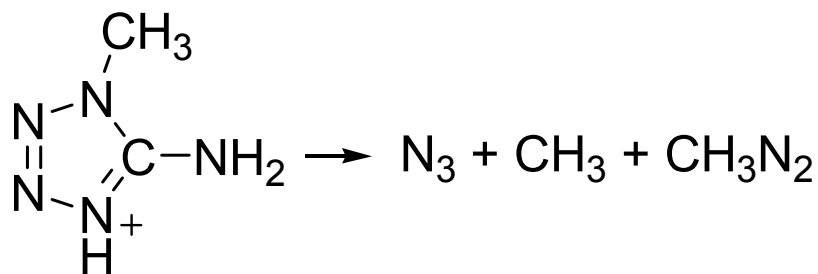
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1,5-diamino-4-methyl-1H-tetrazolium dinitramide

The structure for MeDAT_DN is given in **12**. In Figure 6 we again see peaks 44 (NO_2) and 57 (CH_3N_3), as well as a significant increase in the intensity at m/z 28. Again it is likely that the main mechanism for decomposition is that seen in **2**. As previously noted, this mechanism will produce a peak at 57 and an intense peak at 28 as seen with 5-aminotetrazole. For the dinitramide anion we see the production of both N_2O and NO_2 at a similar starting time indicating that the two dinitramide mechanisms are present in this decomposition.
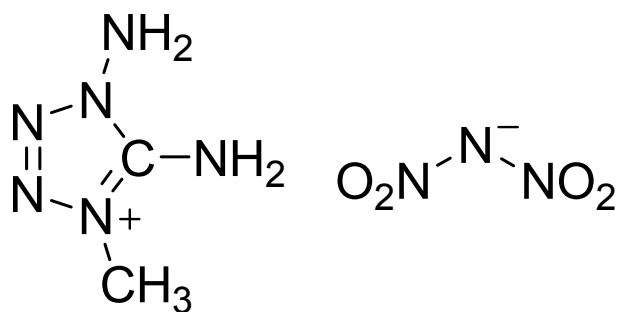
12

One main difference in the decomposition between this molecule and the HAT_DN molecule is that this reaction occurs much faster than HAT_DN. If we take the full-width half max of the detected product species as a representative burn time for both reactions, **12** burns 2-3 times faster than **5**. With the decomposition of **5** we were able to observe multiple steps in the reaction where NO_2 appears prior to N_2O. In the decomposition of **12** the reaction happens at a much faster rate and NO_2 and N_2O appear simultaneously and relatively early. However, it can be seen in Figure 7 that N_2O production does peak later than NO_2. A peak at m/z 15 again suggests that the C-N bond holding the methyl group to the ring is easily broken. If we compare the decomposition temperature of the three dinitramide containing materials in Table 1 with their reaction products, we observe that N_2O is observed in MeDAT_DN, and HAT_DN, with decomposition temperatures 833 K and 683 K respectively. However, N_2O is not observed in the decomposition of MeHAT_DN, which has the lowest decomposition temperature of 633 K. This evidence further confirms the previous assumptions of a high and low

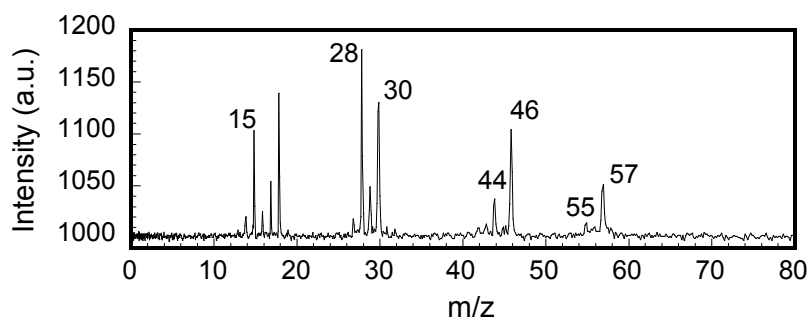temperature decomposition mechanism for the dinitramide molecule.

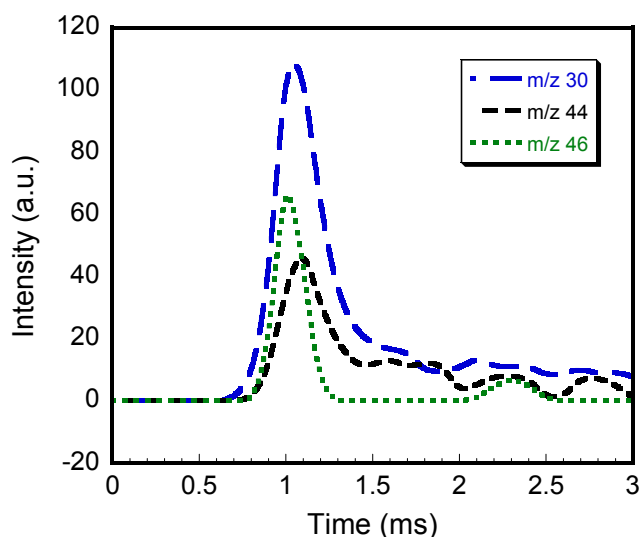**Figure 6:** Detailed mass spectrum of MeDAT_DN, **12**.

Figure 7: Detected product species during heating of **12**.

The gas phase decomposition products of MeDAT_DN were also investigated by Fischer and co-workers using mass spectrometry and FT-IR spectroscopy at a 4 K/min heating rate.[9] From the decomposition products, they predict that the tetrazole ring decomposes to form HN_3 as in **9**, rather than forming N_2 as our results suggest. It is likely that the significant difference in heating rate in our experiment altered how the molecule decomposes. Several species observed by Fischer are not likely present in our study including methyl azide (m/z = 57), $MeONO_2$, and 1,3,5 triazine (m/z = 81, not detected in our study). Although we do observe m/z 57, we do not believe it to be due to methyl azide, as the methyl group appears to break off as indicated by the presence of m/z 15. We also see m/z 57 for molecules that do not contain methyl groups, suggesting this peak is due to CH_3N_3. Fischer's study detected the methyl azide through FT-IR spectroscopy, but did not detect CH_3 (m/z 15) in their mass spectrometer. Since 70 eV ion sources are used in both experiments, m/z 15 in our study is not due to fragmentation of methyl azide, as it would be apparent in both works. This argument holds for the

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absence of MeONO$_2$ in our high heating rate study. The MeONO$_2$ was identified through FT-IR spectroscopy by Fischer, but m/z 46 was not detected. This suggests that the presence of NO$_2$ in our system is due to a different breakdown mechanism of the dinitramide molecule that does not involve the formation of MeONO$_2$.

1,5-diamino-4-methyl-1H-tetrazolium azide

Aside from dinitramide containing salts, we also investigated the tetrazole containing cations with various other anions. The spectrum for MeDAT_N3, **13**, is shown in Figure 8.
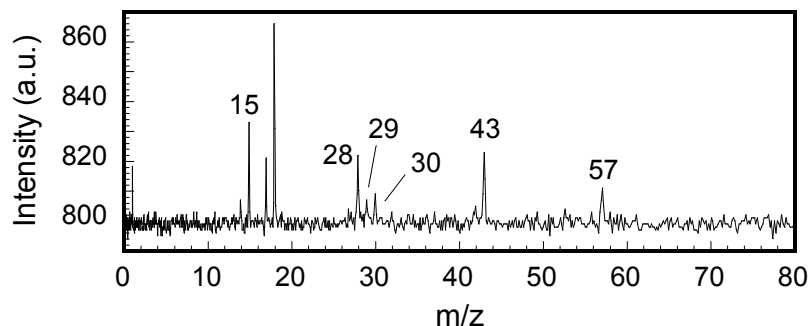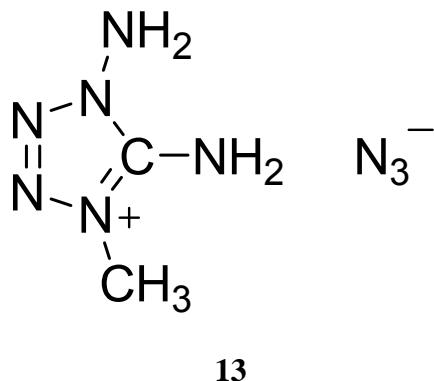
Figure 8: Detailed mass spectrum of MeDAT_N3, **13**.

13

The decomposition for this material is similar to what was seen for the previous material **12**. We see the evidence of the nitrogen expulsion mechanism with peaks at m/z 57 and 28. Peak 43 in this case can be attributed to the protonated azide structure HN$_3$. When comparing this material with MeDAT_DN we would expect MeDAT_N3 to show a lower thermal stability.[6] This appears to be the case as we see decomposition temperatures of 833 K and 583 K for MeDAT_DN and MeDAT_N3, respectively.

1,5-diamino-1H-tetrazolium nitrate

The structure for DAT_N is shown in **14**. This material is slightly different from the other tetrazoles examined thus far as it is a diaminotetrazolium cation without a methyl group and is also paired with a nitrate
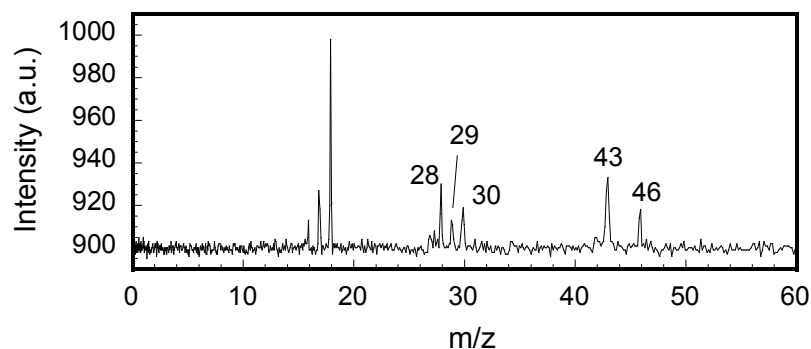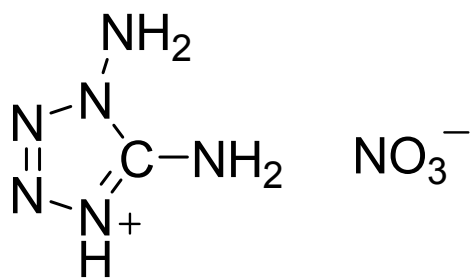
anion.

Figure 9: Detailed mass spectrum of DAT_N, **14**.

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From examination of the breakdown mechanisms of each of the other materials, there appears to be a trend in how the tetrazole molecule will break apart based on the placement of the functional groups around the outside of the tetrazole ring. Molecules **12** and **13** both have functional groups symmetrically placed around the tetrazole structure, whereas **10** has the methyl group on one side of the ring. The decomposition of the tetrazole ring for **12** and **13** follow the same pattern of N_2 expulsion, and molecule **10** produces HN_3. Following the logic that the placement of the functional groups have an important role on the tetrazole ring breaking, it would be expected that DAT_N would decompose in a similar fashion as structure **10**. From Figure 9 this mechanism is confirmed as there is a large peak at m/z 43 representing HN_3 and the absence of peak 57, which is representative of the N_2 expulsion. We also observe peaks at m/z 46 and 30 which can be attributed to NO_2 formation from the nitrate anion.

μ-DSC

To determine activation energy, several of the materials were tested using a μ-DSC system. For each material the decomposition temperature increased with the heating rate in a linear fashion. In varied heating rate experiments it is possible to extract kinetic parameters using the Kissinger Method.[12] Figure 10 shows the data

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plotted Arrheniously demonstrating a minimum correlation coefficient greater than 0.92 for each set. As previously mentioned, most of these materials are synthesized by the Klapötke group at Ludwig-Maximilian University of Munich. Aside from synthesis, this group executes a variety of performance tests on these materials; therefore much of the work presented here will be compared with their slow heating experiments. Since each of these materials show differences in their dependence on heating rate, each will be discussed separately.
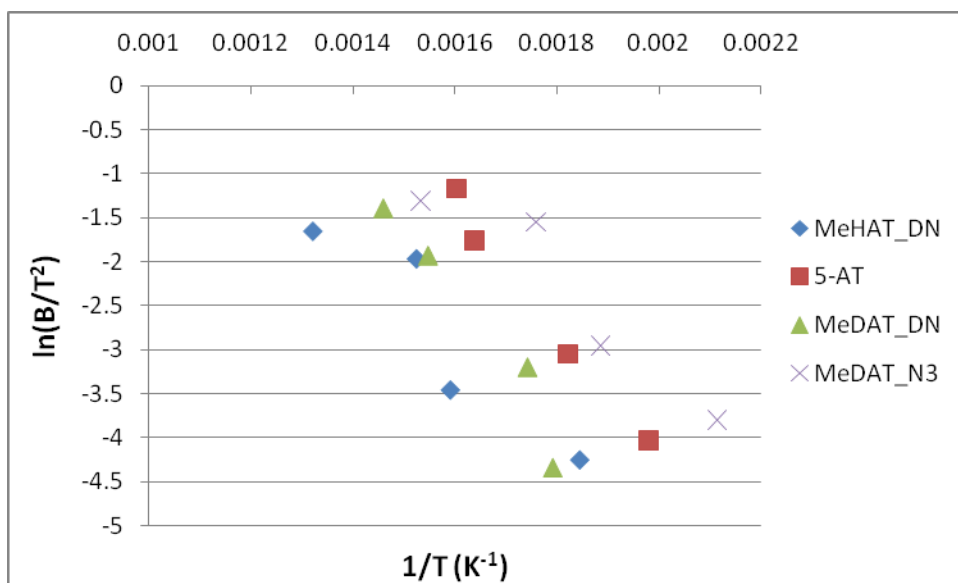

Figure 10: Plot of the Kissinger Method for each sample. The slope of a line through each set is proportional to the activation energy.

MeDAT_DN

A sample trace for MeDAT_DN with a strong exothermic peak is shown in Figure 11a. This is consistent with traditional DSC experiments, which also show a strong exotherm with a peak shift from (450 to 488) K for a (2 to 40 K/min heating rate range .[9] The variance of decomposition temperature for the high heating rate micro-calorimeter occurs in the range of (558 to 685) K. The elevated decomposition temperature in our experiments was a result of the use of high heating rates. Traditional DSC experiments also indicate a melting point at 358 K which is not apparent here. It does appear that there is a broad shallow endotherm that leads up to the exothermic event, which may be indicative of melting, but this is not conclusive at each heating rate. The activation energy was based on the peak of the exothermic event and calculated to be ~68 kJ/mol, more than half of the ~138 kJ/mol calculated by Fischer et al through both the Ozawa and Kissinger methods with very little

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difference between the two.[9]

MeDAT_N3

MeDAT_N3 is reported to show an endothermic peak in the range of (458 to 484) K for various heating rates, and has a reported melting point of 408 K.[9] In Figure 11b a large endothermic peak is observed for this material, which is consistent with the low heating rate work.[9]
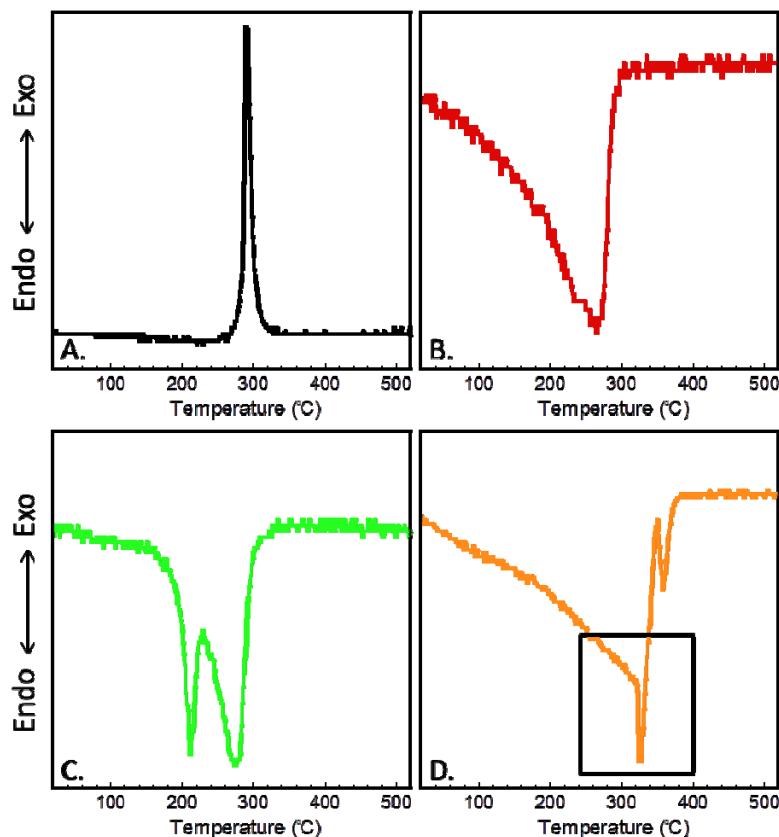

Figure 11: Microcalorimeter traces with a 13,000 K/s sec heating rate for A) MeDAT_DN, B) MeDAT_N3, C) 5-AT, D) MeHAT_DN.

With the rapid heating rate used in this experiment the peak of the decomposition ranges from 473-653 K. Again, using the Ozawa method the activation energy is calculated to be ~38 kJ/mol, compared to 107 kJ/mol in the previous work. The main difference between the high and low heating-rate calorimetric traces is that the low heating rate displays a very broad endotherm. We believe this endotherm is a result of both sublimation and decomposition, which at lower heating rates is observed as two endothermic peaks. Experimentally, the main variation between the previous work and the present study was that the previous experiment is performed in a

semi-enclosed container which has a 1 µm hole in the top to release glass, and the present work was done in an open environment. Fischer and co-workers mention that if they use a completely closed container then the two endotherms become one. It is possible that in our experiment, we were heating at such a rate that the sublimation and decomposition were happening as one process as well. Note that in the previous work the samples showed mass loss at a fairly low temperature of 378 K; however there was no DSC signal at this temperature. It is possible that an increased sensitivity was gained with the small size of our microcalorimeter and that the early mass loss is actually an endothermic event that could not be detected. Another possibility is that the sample solution was evaporating before the energetic material has a chance to react. For this to happen the energetic material would need to dissociate and form a solution with a relatively high vapor pressure. However, we do not expect this to happen as the energetic materials used in this study are stable in H_2O and ethanol, and the ionic salts are known to have low vapor pressures.

5-AT

5-AT is the one material of this set that is a neutral material rather than ionic. However, it is tested here as it is the back bone of the cation species in each of the other EMs. This sample at 10 K/min displayed a decomposition temperature of 480 K and has a melting point of 478 K.[3] The activation energy was also reported to be (136 to 153) kJ/mol using several different iso-conversion methods for heating rates of (0.63 to 40) K/min. Figure 11c shows a sample trace for 5-AT using the high heating rate microcalorimeter showing two endotherms, the first of which peaks at just over 473 K, that we attribute to melting, and the second we consider to be the decomposition. The melting of 5-AT occurs between (478 to 493) K consistently for all heating rates, but the endothermic peak increases with heating rate in the range of (505 to 624) K. In the previous work only one major endotherm is observed during DSC experiments, but it is possible at slow heating rates that these two processes happen fast enough that they could not be distinguished separately. The peak temperatures from the second 5-AT peak were used for kinetic analysis and the activation energy was found to be ~61 kJ/mol. This activation energy is about half of that previously reported, but is reasonable considering the significant difference in heating rates in the two experiments.

MeHAT_DN

Traditional DSC traces on this sample at 5 K/min show an endotherm due to melting starting at 363 K and an exotherm starting at 418 K.[1] In the micro-DSC studies the thermal trace of Me-HAT_DN in Figure 11d can be broken down into several reaction steps. First, a slow endotherm starts shortly after the heating and is similar in nature to the endotherm in Me-DAT_N3 in Figure 11b. Secondly we observed a sharp endotherm, shown in the boxed region of Figure 11d, which is quickly followed by an abrupt change in direction toward the exothermic region of the figure. This endothermic peak occurs in the range of (541 to 756) K. We believe that the sharp endotherm and exotherm are two separate events. The narrow exotherm does not provide quite enough energy to create a net negative change in enthalpy. The appearance of multiple peaks is consistent for most heating rates, with the exception of the slowest heating rate. For kinetic analysis, the peak temperature of the last peak was used, assuming that at low heating rates this second peak was not distinguishable from the first peak. The activation energy was found to be ~44 kJ/mol, which is consistent with the other findings of this study.

Conclusion

Using a T-Jump/TOFMS we have studied the thermal decomposition of several tetrazole containing energetic salts under conditions that minimize secondary gas phase reaction. By examining several different variations to the cation structure, we were able to draw some conclusions about the decomposition pathways of the tetrazole ring. It is clear that there are two different reaction pathways demonstrated for the tetrazole ring in this work. Both pathways decompose through a breaking of the tetrazole ring, one with the expulsion of molecular nitrogen, the other producing HN_3. There was not significant evidence in this study to suggest that the reaction pathways played a major role in the decomposition temperature of the materials, however there is correlation between the placement and composition of functional groups and the breakdown of the tetrazole ring. MeDAT containing salts materials decomposed via the N_2 decomposition, while each of the others showed characteristics of the HN_3 mode. There is also evidence shown for high and low temperature decomposition of the dinitramide anion, as dinitramide containing materials that exhibited higher decomposition temperatures, also produced N_2O as a decomposition product, whereas the other dinitramide containing materials primarily produced NO_2. In a separate study we were able to extract the activation energy of several green energetics under high heating rates. Due to the rapid heating of these samples, significantly lower activation energies were obtained, further evidence that we are probing different mechanistic events.

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